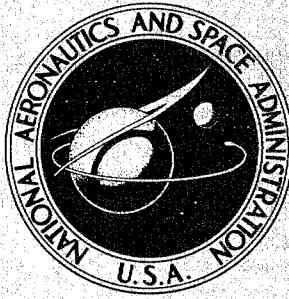


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INITIATION OF
FAILURE MECHANISMS IN
GLASS-RESIN COMPOSITES

AUG. 1966

by William J. Eakins

Prepared by
DeBELL & RICHARDSON, INC.
Hazardville, Conn.
for

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NASA CR-518

INITIATION OF FAILURE MECHANISMS IN
GLASS-RESIN COMPOSITES

By William J. Eakins

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Prepared under Contract No. NASw-1100 by
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Hazardville, Conn.

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FOREWORD

The final report for NASA Contract No. NASw-1100 is issued in two parts. Part I, NASA CR-517, by Richard A. Humphrey is titled "Precision Winding of Cylindrical Composites with Shaped Glass Filaments." The title of the contracted study was "Studies of Hollow Multipartitioned Ceramic Structures."

Mr. Richard A. Humphrey helped with the development of the photographic techniques and Mr. Cecil Paskewitz did the experimental work.

ABSTRACT

[The "state of the art" in failure mechanisms of glass-resin composites is summarized, analyzed and advanced. A new theory is presented to correlate existing data.

In Appendix A, the value of flat-sided rectangular microtape as a strain-measuring device is considered and pictures of photoelastic studies on castings are presented.

In Appendix B, the effects on castings of shrinkage and external loading are analyzed.]

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INTRODUCTION

This work is a continuation of the work started under our previous contract with NASA Headquarters and reported in Appendix I of our final report on this program issued by NASA as Contractors Report CR-142 titled "Study of Hollow Multipartitioned Ceramic Structures".

Program Design

The effort on this phase of the contract has been spent along the following lines:

1. An overall rationalization of the geometry of the composite and the stress-producing factors of an internal and external nature.
2. An intuitive estimate of the stress-concentrating factors.
3. Observation and measurement of these stress-concentrating effects in various manners in an effort to pinpoint their location and magnitude.

The methods used are:

1. Measure resin shrinkage vs. casting size and shape.
2. Examine the square corners of castings to determine the effect of geometry on strain concentration.
3. Study the heat release as a function of curing cycle to determine sensitivity of resins to such changes, particularly in how it affects shrinkage.

4. Study the buckling effect in a fiber using glass microtape.
5. Study the effect of compressive loading of a casting on the rate and quantity of water absorbed.

This work must be still regarded as preliminary and a contribution to the overall approach to understanding glass-resin interaction. We have chosen to present it in an overall discussion of the micromechanics of glass-resin composites.

DISCUSSION

When glass fibers are incorporated into a thermosetting resin, there is a well-known stiffening effect; the degree of increase in modulus being directly related to the volume proportion of glass vs. resin in the composite. At low glass-resin ratio, the glass "reinforces" the resin. Even at high glass-to-resin ratios, the resin, although present as an adhesive layer (30% or less by volume), is the continuous phase and must maintain integrity when subjected to a variety of stresses.

Glass filaments in the order of 10 microns diameter have only a tensile property. To be efficiently used, these filaments must be aligned to load with the principal loadings. When the load is applied from more than one direction, which is the usual case, filaments are aligned in more than one direction. It is the resin that maintains these filaments as a mutually-supporting, integrated mass by transferring stress between the fully-loaded, partially-loaded and non-loaded filaments and filament bundles (called strands).

Table I shows the interfacial stress to be expected if the full tensile loading to failure of an E glass filament were transferred from the filament to the surrounding resin maintaining contact with only one inch of the filament length. It can be seen that these values are nominal and that a good mechanical bond should readily transfer this level of interfacial loading unless a condition exists that causes the loading to pass in a marked non-uniform manner from the glass filament to the matrix resin.

TABLE I
The Transfer of Stress from Filament to Matrix

Filament Loading: 500,000 psi
Length of Matrix-Filament Contact: 1 inch

| <u>Size Code</u> | <u>Diameter, 10^{-3} inches</u> | <u>Tensile Loading 10^{-3} pounds</u> | <u>Interfacial Stress, psi</u> |
|------------------|--------------------------------------------------|--------------------------------------------------------|------------------------------------|
| B | .14 | 7.7 | 17.5 |
| E | .28 | 30.8 | 35.0 |
| G | .37 | 53.5 | 46.0 |
| K | .53 | 111.0 | 70.0 |

Thus, the stress would rise in the resin at or near limited areas of the glass surface. It will be shown that geometrically-related highly stressed, very limited areas of this type do exist as described.

Poisson's Ratio and Shrinkage Effects

Differences in Poisson's ratio will contribute to the stress at the glass-resin interface and in the matrix of a glass-resin composite material.

The contraction in a plane normal to the application of a tensile force divided by the tensile elongation gives Poisson's ratio. Glass has Poisson's ratios (PR) in the order of 0.18 to 0.20, while in laminating resins they are 0.30 to 0.38. The effect of the PR is opposite in low glass as in high glass composites. When a glass filament is surrounded by resin, a tensile stress parallel to the glass fiber will cause the resin to contract more than the glass and create a compressive radial stress. Where the glass content is high, as in the center of a multifilament strand, the resin is surrounded by glass. This second system under the same tensile stress will tend to develop tensile stresses in the resin because the resin will be contracting as before to a greater degree than the glass but instead of contracting to the glass apparently will be trying to pull away from it. Thus, a composite may have some high glass regions with tensile radial stresses due to Poisson's ratio and other regions may be under compressive radial loading due to this PR effect.

Thermosetting resins; be they polyesters, epoxies, phenolics, melamines or silicones, all have one marked characteristic. During the curing and cooling of the resin to the state in which it is used, the resin increases in density or, by increasing its mass per unit volume, the resin shrinks. A number of investigators (1, 2, 3) have illustrated the importance of this property. Some shrinkage would appear beneficial since it causes the resin envelope wetting the glass fiber to grip the glass fiber more tightly. Shrinkage is natural to expect for polymerizing resins going from a liquid to a solid state. It is very difficult to study in glass-resin materials due to their micro-

scopic state of subdivision and the likelihood that the critical strain patterns are on a sub-microscopic scale. The instrumentation is yet to be developed for such investigations.

Distribution of Shrinkage Stresses

The shrinkage to be expected in a resin is influenced by both the size and shape of the resin and the surfaces with which it is in contact. In a glass-resin material, the density of the resin is likely to vary throughout. The resin should shrink to the least degree between the filaments of a strand. The bond of the resin to the glass, the reduced resin to glass volume and the high modulus and the heat absorbing value of the glass all combine to cause this effect. However, between non-parallel strands, resin-rich regions appear where the resin to glass volume markedly increases. In filament winding, layers of resin appear when the direction of winding is changed. In glass fabric laminates, there tends to be resin layers between yarn bundles and between the layers of fabric. In these regions, the resin is much more free to decrease in volume. The geometry is favorable and slightly higher temperatures may be realized in the self-heating resin due to its much higher volume per glass contact area. Thus, there should be a strain pattern in the resin matrix due not only to the shrinkage of the resin and the geometric factors involved but also due to the variation in the increase in density.

Various resins show great differences in density going from the liquid to the solid state and returning to room temperature. They are also greatly

affected by the mass/unit area of exposed surface. Table II gives a comparison of four interesting resin combinations measured in this current work.

Note that while formulation is a most important criterion, the size and/or shape can have a marked effect, particularly in high shrinkage formulation resins.

Figure 1, a photograph taken with polarized light of a 1/2" x 1/2" x 1" casting, suggests the high level of stress on the end faces as compared to the side faces of this casting. This work (4) suggests that the high stress is confined to within less than a thirty-second of an inch of the end face. The strain pattern is a result of the stiffening effect of the edge and the corners of the casting creating narrow regions of stress concentration on the end face.

TABLE II

Changes in Density of Resin Castings on Curing and Cooling to Room Temperature

| Formulation | Density of Resin gm/cc | 1/2 x 1/2 x 1" Casting Density gm/cc | Shrinkage % | 1/8 x 1/4" Casting Density gm/cc | Shrinkage % |
|----------------------------------------------------------------------------|---------------------------|-----------------------------------------|-------------|-------------------------------------|-------------|
| 1. Epoxy - E-828, 41 pph MNA 0.6 pph BDMA Cure Cycle A* | 1.188 | 1.215 | 2.22 | 1.205 | 1.41 |
| 2. Epoxy - E-828, 91 pph MNA 0.6 pph BDMA Cure Cycle A* | 1.198 | 1.228 | 2.44 | 1.228 | 2.44 |
| 3. Epoxy - ERRA-0300, 28.7 pph MPDA Cure Cycle B* | 1.164 | 1.273 | 8.56 | 1.248 | 6.73 |
| 4. Polyester - P-43, 11 pph Styrene 1 pph Bz_2O_2 Cure Cycle C* | 1.077 | 1.225 | 12.08 | 1.194 | 9.80 |

* See Appendix A, Table A-1

Many investigators (5, 6) have shown the relationship between the heat given off by a resin vs. time during curing and the physical properties of resulting laminates. Some resins are very sensitive to heat during certain periods of the curing cycle. Figure 2 illustrates the effect of a 10-15°F change of one critical step during a four step cycle.

The resins that show high sensitivity to changes in the cure cycle are generally those showing high normal shrinkage. The ERRA-0300/MPDA resin, whose relative exotherm curves are shown in Figure 2, has a shrinkage in small castings in the order of 6-8%. It is likely that the relatively high exothermic heat of such resins produces the additional shrinkage on cooling down to room temperature. Filament wound products like rocket motor cases have been shown by photomicrographs of cross sections to have regions that change by a factor of three or more in resin concentration. It should be suspected that when resins with high shrinkage are used, the shrinkage of the resin will be higher by possibly 25% in these high resin regions, producing a strain variation and stress concentration where the resin of the high and low concentration levels meet.

Stress Due to Absorbed Gases (Water)

In the laminating resin, besides the shrinkage, there is also the effect of absorbed gases and liquids to consider -- the most serious of which is water. Absorbates tend to swell the resin phase; thus, absorption due to this effect will vary within a casting of resin or a composite of the resin with

glass. The degree of swelling will depend upon the degree of freedom within the resin. Consider moisture and water vapor as examples. The water will absorb to the degree allowed by the geometry of the resin casting or matrix and the rigidity of its confinement. For example, a resin cast and bonded to form a layer on a ball of glass on exposure will not absorb the same magnitude of moisture as the same volume to surface area of cured resin not bonded to the glass ball. Contact with the ball reduces swelling and remarkably reduces the rate and amount of water absorption.

Cured thermosetting resins are also affected by changes in ambient temperatures. Resins in castings having low moisture absorption (1% at room temperature) may increase their equilibrium moisture content as measured on this program by as much as 30% by an increase in temperature in the immersion water of 10°F. (See Appendix B)

The formulation of a thermosetting resin directly affects the moisture it will absorb. As the hydrocarbon nature of the resin is modified through the increasing addition of oxygen or nitrogen, the water absorption is increased. Ether linkages are especially effective. In formulations where the moisture absorption is high, it is possible to develop such high local stresses within a casting of the resin or the matrix of a composite that the polymer develops fractures and rips apart. Thus, if a high moisture absorption resin, like a general-purpose polyester, is used for the laminating resin, there must be an excellent bond to the glass fiber to limit the swelling of the resin and,

thereby, the amount of moisture it will absorb. Measurements made in this laboratory (4) have shown that properly applied and properly chosen coupling agents will produce this controlling effect.

The above discussion indicates that the matrix in a glass-resin combination material may receive stress from a number of effects. There are the effects of the applied stress itself; of Poisson's ratio; of shrinkage; of varied exotherm; and of absorbates, particularly water. It is suggested that these effects do not result in an even application of stress throughout the matrix but instead the effects themselves and the strains they cause produce localized stress concentrations that can become critical when the remaining regions are in only a lightly-loaded condition.

Stress Concentration Factors

It has been shown by Outwater (7) that the shrinkage of resin in a "tricorne" of resin formed and bonded between three tightly-packed glass tubes will produce stress concentrations at points on the glass surface. Figure 3, taken of this model by polarized light, shows an isochromatic fringe pattern. The arrows on the photograph indicate those positions at the resin-glass interface where the fringes have highest frequency indicating the points of highest stress concentration at the glass surface. Outwater states that he has estimated the stresses as high as 5,000 psi at these points or lines extending in an axial direction from the glass filament surface. At high glass content, such as exists between the filaments of a strand, the PR

effect will increase the intensity of the shrinkage effect. The tensile stress from this PR effect will not be uniform along the glass-resin interface but will be highest in the area about the midpoint of the wall of the "tricorne". It will, therefore, further intensity the high strain areas in the matrix at the glass-resin interface.

Shrinkage of the resin also produces buckling stresses on glass fibers. McGarry (8) and Dow & Rosen (9) have shown the differences in strain pattern in a resin cured around a circular filament. McGarry shows that the filaments buckle helically and where two fibers buckle and the fibers cross, there is an interaction of the stress fields around the buckled fibers. Dow and Rosen have shown that the diameter of the fiber changes the node of buckling curve.

In this work we have used a single 0.0006" diameter microtape*, 0.020" wide, as the buckling fiber. When the sufficient stress is applied by further curing of the resin and thermal contraction during cooling, the microtape will buckle, collapsing on the short dimension to give a series of ripples (Figure 4). As Dow and Rosen found with circular fiber, we have found that the node of the fiber is a function of microtape thickness. However, we have found that the amplitude of the ripple will vary from a very slight deviation from straight as shown in Figure 5 to the considerable deviation shown in Figure 6. These last two photomicrographs were taken using the light from crossed polaroids to develop the strain pattern in the resin.

* A study of the photoelastic effect of a single microtape embedded in a casting is given in Appendix A.

There are, therefore, two known causes for micro-regions of stress concentration in high density composites with layers of parallel circular filaments. The first is the shrinkage of the resin surrounded by a pointed roughly triangular periphery of glass causing high stress concentrations on the periphery. The second is the effect of shrinkage on the thin long glass cylinders causing the cylinders to buckle. Although the two effects appear additive, they are not. The first comes to a peak as the filaments approach a tight hexagonal packing. The second becomes more critical as the filaments are more widely spaced and the volume change of the resin vs. the glass becomes more pronounced.

Micelle Theory

Before considering the stress pattern in the interface region, the physical nature of the polymerized thermosetting resin must be considered. The glass and resin being amorphous materials have both been found to be composed of micelles or high modulus "Kernel" phase surrounded by a lower modulus continuous phase. The resin micelles may be visualized as relatively high molecular weight (in the order of 5×10^8 atomic mass units) closely-packed masses that have the reacted groups at close to the minimum allowable distance apart. The lower modulus continuous phase is believed to be composed largely of lower molecular weight polymer that has poor atomic packing and a lower bond density. Erath and Robinson (10) have found that diallyl phthalate, epoxy, phenolic and silicone resins have a micelle size averaging 800 - 900 Å. Their technique consisted of splitting a casting of cured resin, making a platinum-carbon replicate of the exposed surface and making

an electron photomicrograph of the replicate. The micelles were clearly evident (Figure 7). The crack propagates through the continuous low modulus phase rather than through the micelles with their more favorable atomic packing and higher bonding density.

Crack Propagation

McGarry and Selfridge (11) have shown that it takes a magnitude or more of energy to propagate a crack through a cured thermoset resin polymer than through a linear polymer. If the crack is visualized as a peeling through the lesser crosslinked nonplane-like layer, the crack at the tip of propagation must either change direction or the micelle immediately ahead of the tip moves for an instant the $200 - 300 \text{ } \overset{\circ}{\text{A}}$ distance necessary to allow the straight line advancement of the crack tip. An energy of 10^4 ergs/cm^2 is likely to momentarily displace an $800 \text{ } \overset{\circ}{\text{A}}$ micelle having a modulus of perhaps 1×10^6 psi surrounded by a layer having a modulus of perhaps 1×10^5 psi.

From other data in this paper, it may be concluded that the energy required to propagate a crack in a thermosetting resin casting is not related to the number of crosslinks in the cured polymer as might be indicated by an increase in the heat distortion point or change in resin-hardener formulation as in an epoxy resin. This result also suggests that the micelle structure present in amorphous materials may be the dominant factor. Once the micelles are formed in the resin at a relatively low crosslinking density, the potential cleavage planes exist. As crosslinking continues to make a higher

modulus polymer, the work to cause cleavage will (or will not) rise depending on whether (or not) the weaker material surrounding the larger molecular weight stronger elements continues to crosslink and become stronger. It is not unlikely, therefore, that crack propagation in the matrix of a glass-resin composite depends upon the nature of the micelle condition in the cured resin and is strongly influenced by the degree of restraint imposed by its proximity to an adherent glass surface.

McGarry and Selfridge (11) have also presented evidence to show that a crack may be propagated in a thermoset resin casting with approximately one-tenth the energy required to propagate a crack through the resin layer of a fabric laminate made with the same resin. While, as the authors suggest, the structure of the fabric would impose a more torturous path upon the advancing crack, it is unlikely that this characteristic alone furnishes a sufficient explanation. The restraint of the glass fibers (49% by volume) upon the resin near its surface should also increase the work to produce a fracture surface. The increase in energy required to propagate a peel crack in a well-bonded, high glass composite matrix will arise from the increased energy required to move a micelle within a restrained resin layer due to the relative immobility of the glass surface and the bonding of the resin to that surface.

The Glass-Resin Interface

In the light of the background covered above, the interface stress loading problem may be examined in detail. The interface in physical chem-

istry is considered a plane of infinitesimal thickness that bounds a solid or liquid body. There are solid-gas, solid-liquid and liquid-gas interfaces. It is recognized as a plane of discontinuity where it may be difficult to maintain an energy or sometimes a material balance. The surface tension property of a liquid and the spreading property of a soap film on water are all evidences of the phase instability at the interface.

However, in glass-resin composites, reinforced plastics, etc., the glass-resin interface is a submicroscopic region. It may be defined as that portion of the composite that is between the resin and glass and that part of the resin or glass that cannot engage in its normal (Hookean) response to stress to maintain its integrity. The glass-resin interface does not solely consist of the plane of demarcation between the resin and glass but also of the coupling agent, debris of various types on the glass surface, the absorbed water, the surface micelles of glass affected by the water and the immediate resin micelles that must transfer stress yet remain in contact with the glass surface or those resin micelles affected by the contact with the glass surface.

The Stress-Strain Relationship at the Interface Resin Layer

Consider the glass surface and the resin bonded to it. To maintain integrity between the two dissimilar modulus materials, it is necessary that the micelles of glass and resin immediately touching each other exhibit a similar stress-strain relationship. In other words, the resin micelle must decrease its mobility in face of stress loading and act as if it were a micelle

of glass. The glass micelles in contact with the resin, on the other hand, may be able to increase their mobility very slightly to help match that of the resin.

If the resin micelle layer immediately adjacent to the glass is held relatively immobile in the face of stress (i. e., a tensile, shear or compressive loading), it may be considered restrained. Adjacent layers of micelles are decreasingly restrained by the presence of the glass surface until the resin may engage within the restraints of geometry its normal Hookean reaction. It is possible the restraint may have some effect as far as four or five micellar diameters. This theory has been published (12).

If a poor bond exists between the resin and the glass at the plane of contact, failure is likely to occur at the glass surface. However, if there is a strong bond there, failure is likely to occur elsewhere. The glass surface is not smooth in a submicron scale although microcracks and imperfections on the surface contributing to strength loss are considerably larger than these dimensions (13). Zarzycki and Mezard (14) have shown that dust particles and flaws due to water attack on the drawn filament can be in this submicron order of magnitude. Due to this roughness, the glass and first micelle layer of resin will tend to become entwined. Since all stress loading translates into shear stress at the interface, the bond strength to maintain integrity between the cured resin and the glass under these conditions will not have to be as high as the bond strength between resin micelles. A more

complete explanation of this statement follows.

If it be assumed that a high strength carrying bond (by whatever means) exists between the glass and the cured resin, failure under stress is likely to occur in the resin phase in shear no matter how the stress may be applied. Figures 8, 9, and 10 show diagrammatically in the region of the restrained resin layer the effect of tensile, compressive or shear forces. Each force produces a variable rate of change of strain in the restrained resin layer. This effect, the same for each type of application of force, is illustrated (Figure 11) as the application of a shear force across the interface (Figure 10) and the effect of the resulting shear strain producing a concentration of stress at a point estimated as more than two but less than six micelle diameters from the glass surface. Whether a tensile, compressive or shear force is applied, there is a maximizing of stress at a similar plane within the restrained resin layer. It is within this plane of maximum shear stress that failure can occur producing a flaw separation between two adjacent micelles. This flaw, if it be subjected to peeling forces, can grow to become critical to the failure of the composite.

Critical Flaws At the Interface and Their Propagation

It has been shown earlier how the stresses can be concentrated in the resin at very small areas of the interface. It is in one of these areas that a flaw may appear. It will be in a plane parallel to the glass surface. If this flaw was caused by a radial tensile force, the continued effect of this force

will be to cause the flaw to open up through peeling and, if the peeling continued, to fail the piece. Variations in fatigue in parallel filament wound rings subject to static or variable loading must be related to the difference in the rate of formation of the above-described shear flaws and those flaws that become critical or failure-producing through the peel mechanism. Rapid loading rates will produce relatively few flaws in number but a high number of critical to initial flaws in the group. On the other hand, slow or light variable rates of loading should produce the opposite effect. This is why the appearance of the failure region at high glass loading is so different in widely different loading rates.

It should require more energy to propagate a crack (by peeling) when the region through which the crack passes is the restrained resin layer. When a crack is propagated through a resin casting (Erath and Spurr (15) for example), the crack passes between micelles. Since peeling relieves tensile stress by proceeding in a plane normal to that stress, the crack will continue in a relatively smooth curve on a microscopic scale and the micelles must move $100 - 300 \text{ } \overset{\circ}{\text{A}}$ to allow the crack to advance through the non-micelle region. This movement of the micelles requires a high energy potential. Micelles may move upward or downward to allow the crack to advance in a straight line in a resin casting. As the crack passes on, the micelles will return to their original relative locations.

However, when a crack is propagated within the restrained resin layer, there is a limitation in the micelle movement in the direction of the

glass. Only the micelles moving away from the glass are relatively unrestrained. Thus, these latter micelles must move on the average at least twice as far as those in the casting and, therefore, considerable additional energy must be required per unit extension of the crack through the restrained resin layer. McGarry and Selfridge (11) have shown that it takes about ten times the energy to propagate a crack through a glass fabric laminate as through a resin casting of the same formulation and cure. It may be that the crack propagation through restrained resin layers around the twisted glass filaments are a considerable portion of this increased energy requirement.

Recently (4) it has been shown that a relationship exists between stress within a resin casting and the degree to which the specimen will absorb water. The results suggest that compressive loading decreases the specimen's tendency to swell in water. Sometimes the effect of this relatively mild (30%) loading is very marked (Table III).

TABLE III
Soaking 1/8" Dia. x 1/4" Long Cylindrical Castings in Water
(Compressive Loading)

| <u>Resin Formulation</u> | <u>Cure °F/Min.</u> | <u>Water Absorption, %</u> | | |
|--------------------------|-------------------------|-----------------------------------------------|-----------------|-----------------|
| | | <u>Soaking* in Water Under No Loading</u> | <u>3300 psi</u> | <u>7300 psi</u> |
| A. 100 pts. E-828 | 150/30 | 0.68 | 0.67 | 0.25 |
| 91 " MNA | 200/30 | | | |
| 0.6 " BDMA | 250/15 | | | |
| B. 100 pts. ERRA-0300 | 150/30 | 1.47 | - | 0.38 |
| 28.3 " p-MDA | | | | |

* Room Temperature 10-14 days - equilibrium

Additional data obtained on soaking castings loaded and unloaded are given in Appendix B.

Since in a closely-packed parallel filament structure the resin polymer in the tricorne sections is restrained in swelling by the glass filaments, it is not likely that the resin will absorb the amount of water likely in a small casting. In resins having relatively high moisture absorption values, the effect of this restraint in composites must be considerable. The restraint on swelling of the resin must be greater near the glass surface to which it is bonded. Within the restrained resin region, the percentage of water absorbed should decrease and approach zero at the glass surface.

Contributing evidence that the above-stated theory is correct may be seen in examining some recent work of Roskos (16). Here standard 5-3/4" I.D. NOL rings were made and divided into two sets. One set was soaked in water at room temperature, the other at 150°F. Over a 90 day period, the compressive modulus of the tested rings gradually increased 7 and 9% respectively. The samples at 150°F continued to increase to 11% of the initial modulus and then fall back over 90 days additional conditioning to below the dry value. The further conditioning of the room temperature samples beyond 180 days caused similar regressive behavior.

If the resin micelle layers immediately surrounding the 10 μ filaments absorb a small amount of moisture and the moisture molecules act as a series

of keys to fill the voids in the resin and thus increase the modulus of the micelles to near that of the glass, the modulus of the glass would extend out two or three micelle diameters or about 0.3μ increasing the average diameter about 3%. If the modulus increases as the diameter to the third power, there would be a 9% maximum increase in modulus expected, just about the increase realized in the Roskos work.

The above-described theory rests upon the proposition that all forms of stress loading become to some degree a shear stress in the "restrained resin layer". It has been found that the shear stress in the resin in cast form can be directly correlated with the horizontal shear strength obtained parallel to a nest of parallel resin-bonded filaments (Table IV). It cannot be correlated in tensile or compressive properties.

The test performed on parallel filament wound rings is essentially a short beam flexural test, sufficiently short ($8/l$ or less span-to-thickness ratio) to cause the failure to occur in the neutral plane. (At the center (thickness) of the piece under the central loading bar, a flaw plane appears and peels to one of the ends.) The values are taken from reference (12). (Compressive is directly related to shear strength in the absence of voids only (17).)

TABLE IV

Punch Shear Strength of Resin* vs. Shear Strength in
Parallel Filament Wound Rings

| <u>Epoxy Resin Formulation</u> | <u>Punch Shear Strength of Resin, 10^3 psi</u> | <u>Horizontal Shear Strength of Composite, 10^3 psi</u> |
|--------------------------------|-------------------------------------------------------------|----------------------------------------------------------------------|
| A | 7.9 | 8.0 |
| B | 9.7 | 10.4 |
| C | 12.1 | 11.2 |
| D | 14.5 | 14.4 |

* 0.5 million psi modulus resin, 10 million psi modulus glass
Good bonding between resin and glass

It is also strangely true that maximum strength values in the tension (18), compression (19) and shear (18) values of parallel filament wound rings are found at the same glass content (81-84% by weight E glass - 68-71% by volume). These data suggest that it is more likely that one mechanism is critical for all three rather than three different mechanisms happening to reach a maximum at the same glass content.

CONCLUSIONS

It can be seen that the glass-resin composite is a very complex micro-structure that cannot be dissembled and studied but must be considered in its complex state. Large scale models fail as a method of study because the sub-microscopic effects are lost in the size transition.

The glass filament has been studied and tested for strength outside the composite environment. Coating the filament with a resin does not duplicate the restrained condition of the immediate resin micelles in a composite. The effect of the restrained resin on nullifying the surface flaws on the glass is unknown. In truth, it is not known what the strength of the glass filaments may be in a composite because they do not fail in a simultaneous manner.

The matrix or resin has a similar problem but with a different twist. The modulus of the resin is so low (relatively) that strains are created in the resin from many causes. It is almost impossible to determine the true state of the matrix "in situ" with present-day tools or instruments and properties, such as density or water absorption, cannot be extrapolated.

The entire area is pregnant for future study.

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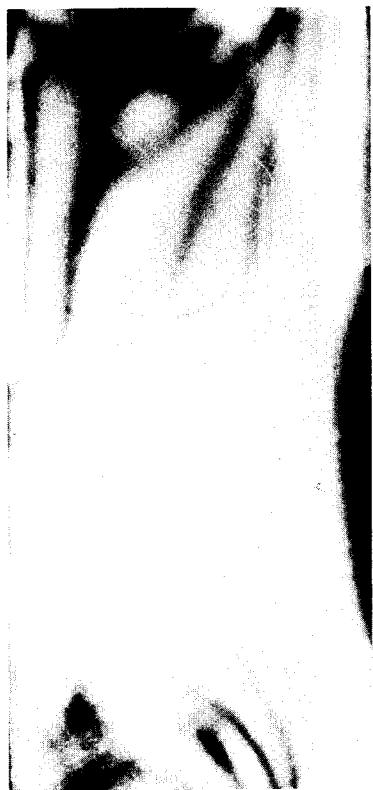


FIGURE 1

A side and an end face of a $1/2'' \times 1/2'' \times 1''$ resin casting taken with polarized light showing the high differential level of strain in the end as compared to the side faces (as indicated by the tightly spaced fringe pattern on the end).

FIGURE 2

The Effect of a Minor Change in the Cure Cycle on the Exotherm Temperature

ERRA-0300, 28.3 pph MPDA

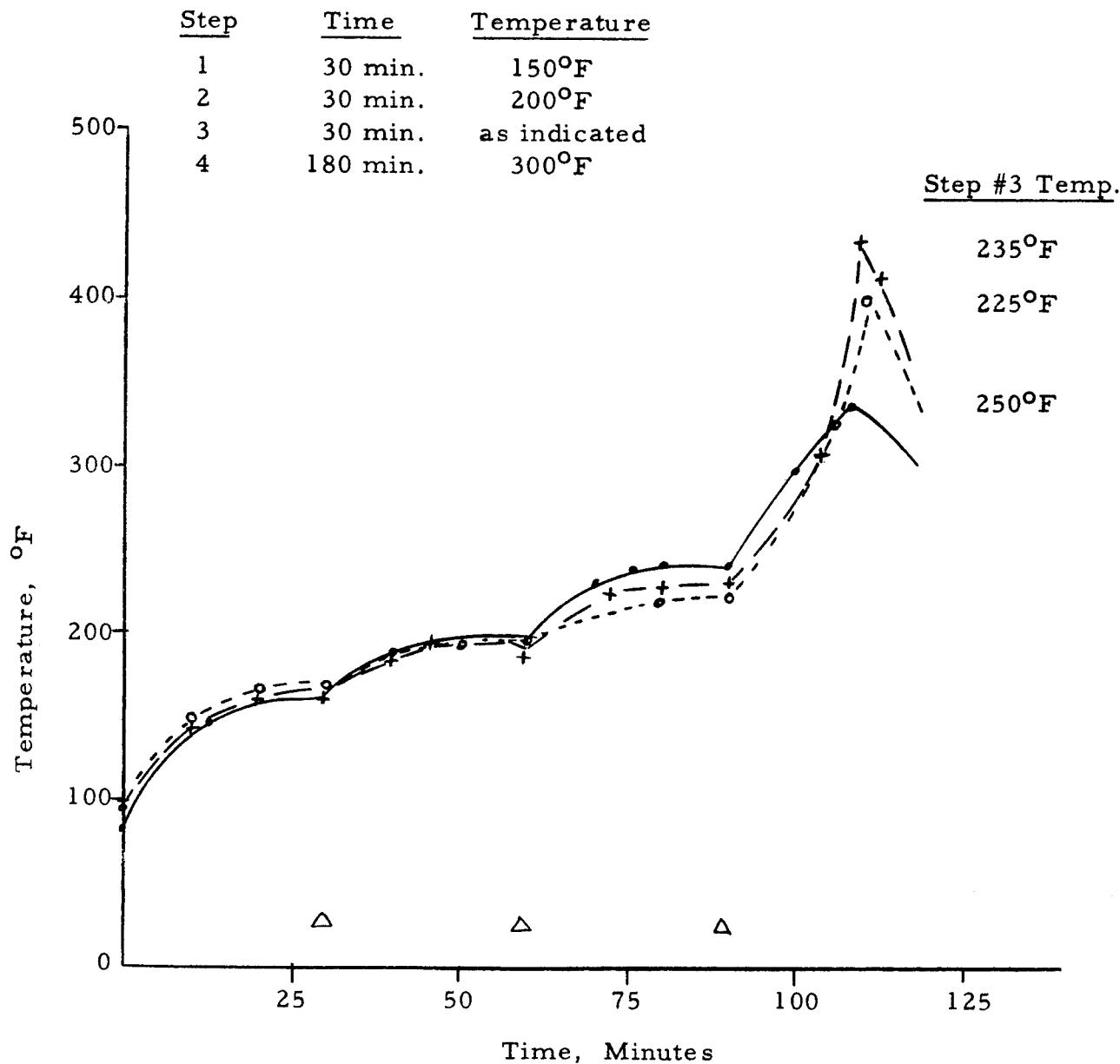




FIGURE 3

The Outwater Effect -- the resin polymer
shrinkage strain pattern between tightly
packed cylinders (Ref. 7)

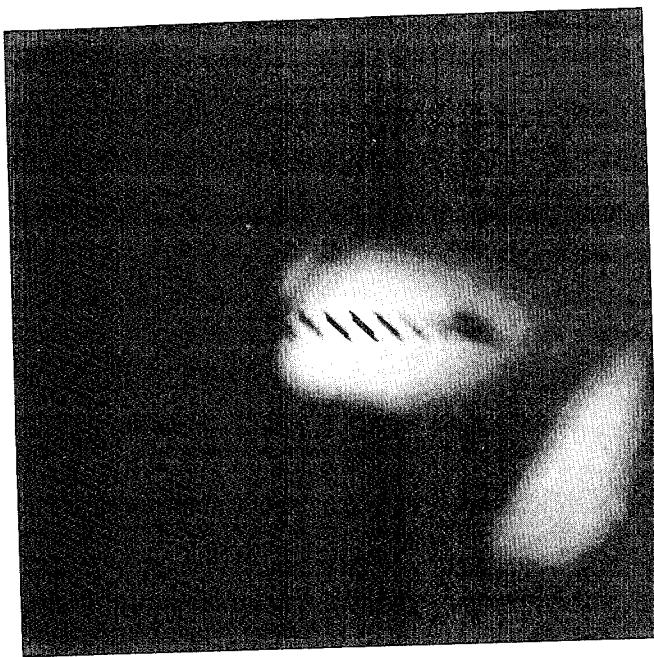
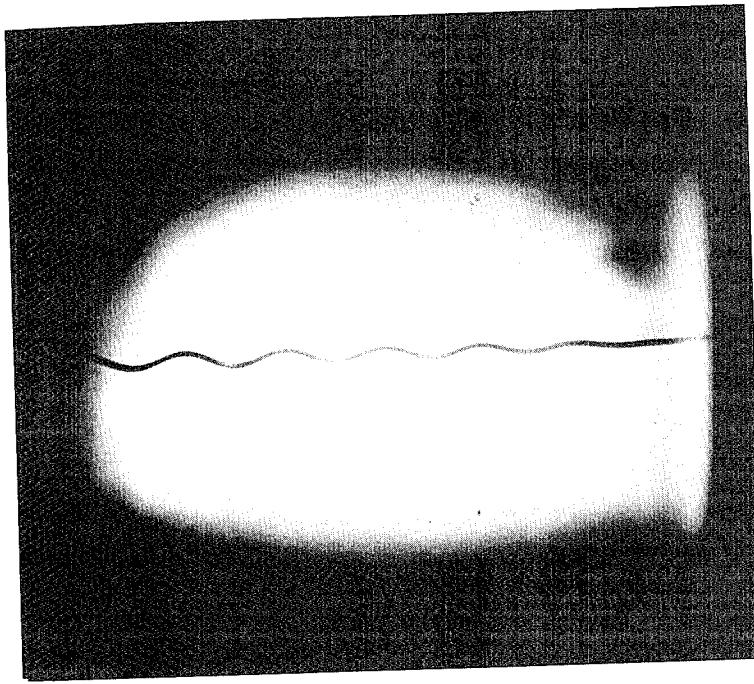


FIGURE 4

The Buckling of Glass Microtape Due to Resin Shrinkage (20X)

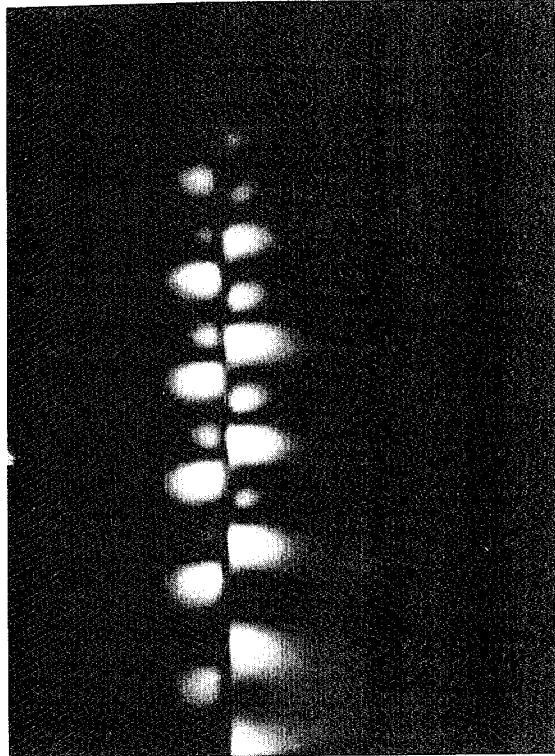


FIGURE 5

Resin Casting with Single Microtape
Viewed Parallel to Microtape Edge:
Slightly Rippled Microtape Caused
by Low Shrinkage Stress in Surround-
ing Cured Resin

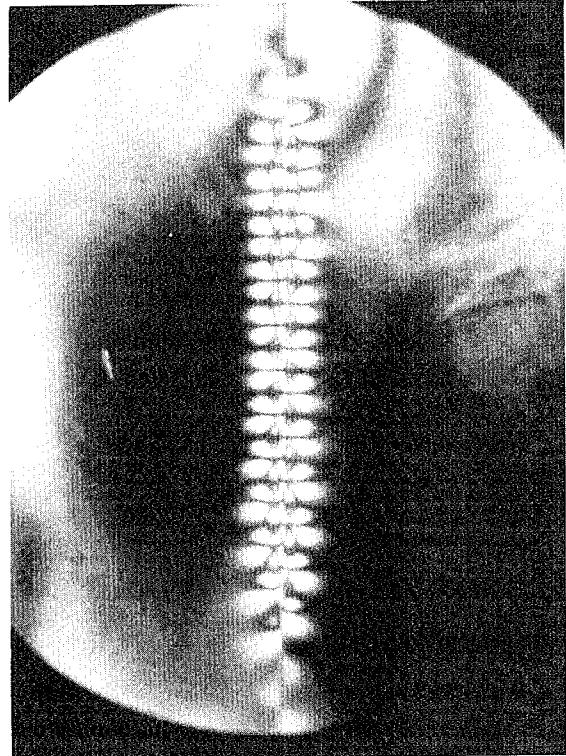


FIGURE 6

Same: Increased Amplitude
of Ripple in Microtape Caused
by Higher Shrinkage Stress in
Surrounding Cured Resin



FIGURE 7

An Electron Micrograph of a Preshadowed
Replicate of a Fractured Surface of Phenolic
Resin Polymer (18,000X)

(Erath and Robinson - Ref. 10)

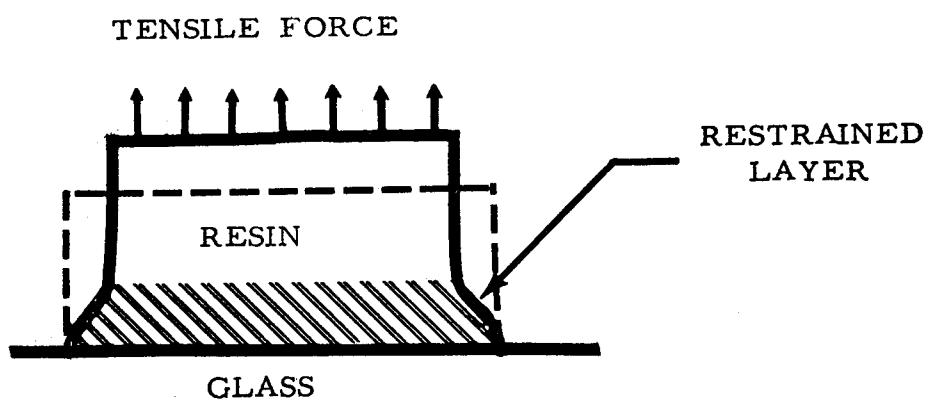


FIGURE 8

The Application of Tensile Stress at the Interface

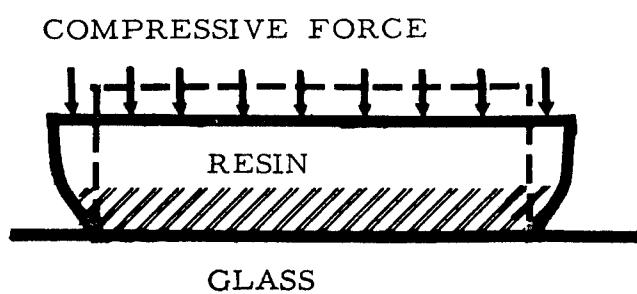


FIGURE 9

The Application of Compressive Stress at the Interface

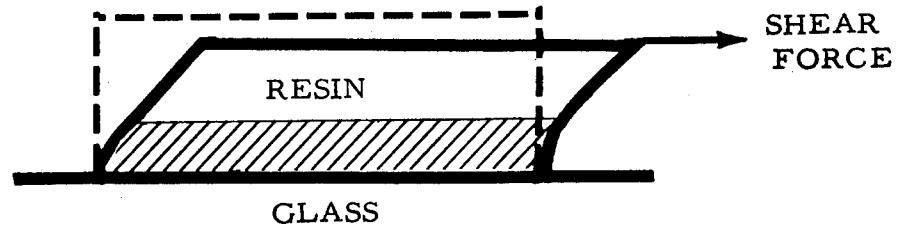


FIGURE 10

The Application of Shear Stress at the Interface

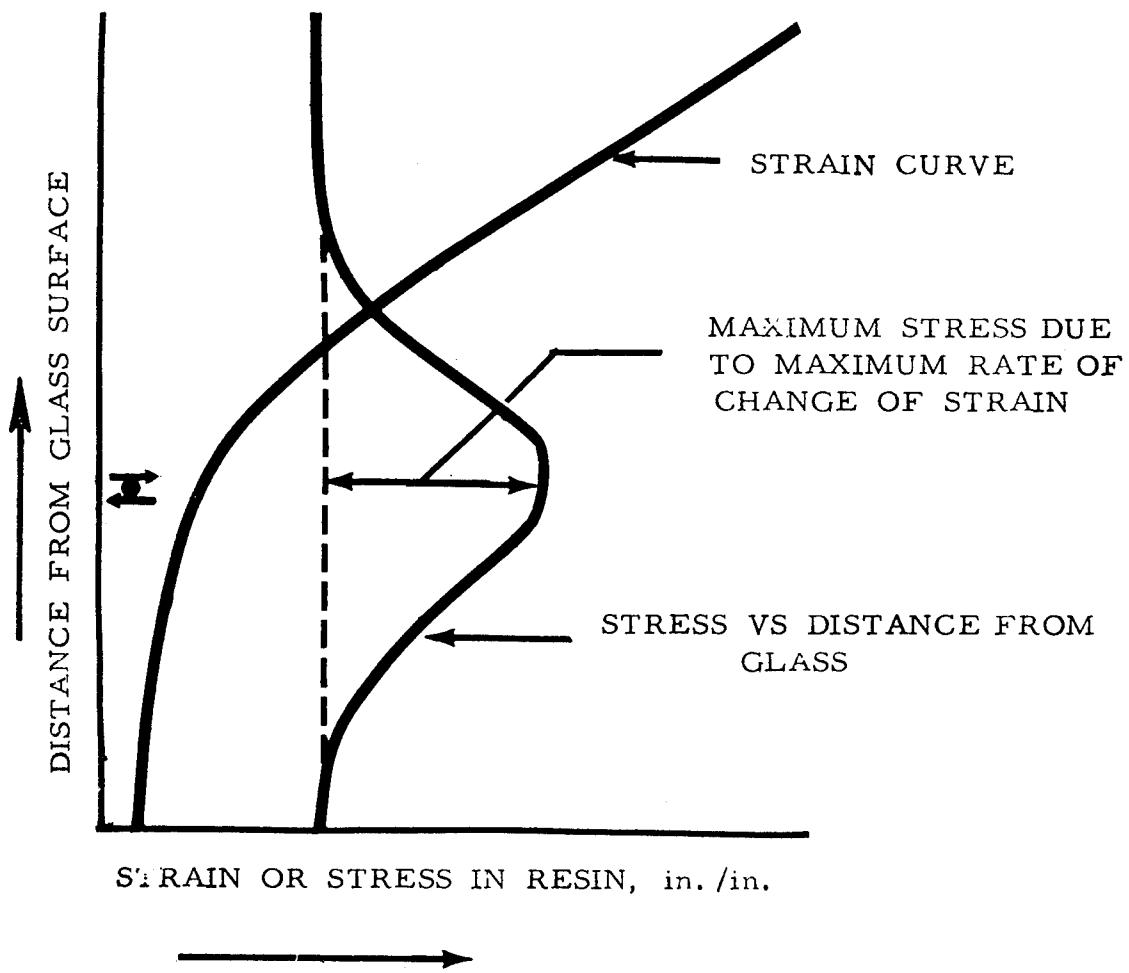


FIGURE 11

The Application of Shear Strain at the Interface

APPENDIX A

The Shrinkage Phenomena of Thermosetting Resin Around Glass Microtape

Laminated glass wound convolute structures using microtape have given high glass density and high modulus values equivalent to the bulk glass, both parallel and normal to the tape direction. However, it has been difficult to improve the strength to give higher values for tube wound forms of more than 50,000 psi circumferential and 25,000 psi axial. Resins of widely varying tensile elongation and toughness are not effective in making marked changes in these values. Orienting portions of the wind in an axial direction are also not effective.

The cured resin layers between the layers of glass in accurately wound structures of microtape of constant width (80+% by volume) are less than 0.5 microns thick as an average. Calculations show that, if no stress concentrations exist, there is more than sufficient glass-resin interface to transfer stress between adjoining layers of bonded tape. It is evident that there are such stress concentrations since the structure is failing at a fraction of the glass loading. In our work, it has been found that flexible resins apparently act rigid when squeezed between microtapes to a thickness of 0.5 microns or less. Also, the more flexible the resin, the more likely the shrinkage will be higher than a rigid resin of the same formulation.

The problem may be looked at another way. If the cured resin layers bonded to the glass microtape are 0.02 mils thick (0.5μ), 60 mils wide and

infinitely long and the overall resin shrinkage is 2%, it seems evident that the resin can (while remaining bonded to the glass) move only in the thickness direction. This would mean moving inward 2% over a distance of five micelles, each micelle being about 0.1μ in diameter. If the micelles next to the glass surface tend to remain relatively unaffected due to their bond to the glass, distortion would be greatest in the middle of the layer (about 3 micelle layers from either side). This distortion may be illustrated in Figure A-1. Although shear stresses will be incurred, particularly between the second and third micelle layers out, a resin with a shrinkage of 2% should only be mildly affected. However, if the shrinkage should increase to 10% by volume (by substituting resins) and this shrinkage be taken over a micelle or two of thickness, it is likely that intermicelle shear failure would result (see page 16).

The next region to consider is on the flat side near the edge of the microtape. Between parallel winds of microtape is a continuous strip of cured resin, roughly the thickness of the microtape and of the width, 1.5 to 4 mils. As shown in Figure A-2, the edges of the microtape are not square but are considerably curved to give a region of transition between the thin resin layer and the bulk resin in the continuous strip connecting four of these resin layers. Undoubtedly, there is greater shrinkage possible in the strip than in the resin layer. However, transition should be possible without stress concentrations if the transitional regions are as indicated.

The buckling effect of slender columns may be another matter with microtape. To investigate this effect, a number of castings were made with a single microtape at the center line of the long axis (Figure A-2). A number of pertinent observations were made and conclusions drawn.

It was found that the microtape tended to ripple in the thickness direction as expected (Figure 4). However, it was not expected that very low stress levels would cause a slight ripple to form. Two degrees of stress level as seen by viewing in a microscope with crossed polaroids are shown in Figure A-4a and A-4b. Neither show very heavy fringe concentrations indicative of high stress loading yet a distinct ripple is present. Increased loading of the microtape in tension up to 50% of full loading did not apparently affect the degree to which the microtape was rippled by the shrinkage.

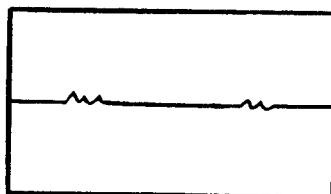
Castings with single microtape embedded were made of approximately the same length and width but with various thicknesses as indicated in Figure A-3. It was desired to study the strains in the castings and the manner in which these strains were reflected in and around the microtape. The resin, E-828 + 91 pph MNA, was chosen for its low shrinkage (between 2 and 3%) and a standard step cure cycle was used of 30 min. @ 200°F, 30 min. @ 250°F and 30 min. @ 300°F. Samples were exposed to air at room temperature to cool. The pattern developed as the specimens cooled. The rippling occurred during the cooling process. Incidentally, 2% glycidoxy propyl trimethoxy silane was added to the liquid resin as coupling agent. It was found

that without this addition, the castings would crack at or near the glass on cooling in the mold.

As shown in Table A-1, buckling of the microtape was noted on the pieces over 0.30" thick, the buckling increasing in length or number of waves as the thickness of the piece increased. The buckling was apparently caused by a stress concentration produced by a shrinkage at the ends. Figures A-5a and A-5b show photomicrographs (25X) taken with crossed polarized light with the thickness of the filament normal to the line of sight. Figure A-6 shows a sketch of specimens indicating the positions of the stress concentrations. The resulting rippling of the glass and the numerous fringes indicating a high stress concentration across the flat upper and lower microtape surfaces.

FIGURE A-6

Diagram at 2X Showing Points of Stress Concentration
in Thicker Castings Cured to 300°F



Note that in Figure A-5b that the stress pattern in the resin has a clear definition that is related to the well-developed stress pattern in the resin at the surface of the glass. The microtape is not buckled either in the center section or to within one-fourth the width of the casting from either end. As the cure was continued at 300°F, the rippling continued to spread across the center section, Figures A-7a and A-7b, but never reached the fringe intensity in the center section as where the rippling first started.

The specimens were then heated to 350°F for 10 to 17 hours to stabilize them at this higher temperature. They were then cooled in air at room temperature. The rippling of the filament and resulting fringe pattern in the resin is shown in Figure A-8 for sample 5. It was found that this fringe pattern could not only be removed by reheating to the top temperature of cure but that the stress relieved condition could be maintained down to room temperature if the specimens are cooled in an insulated blanket. Figure A-9 shows the middle and end section (25X) slow cooled to maintain a stress relieved condition. There is a very low order stress pattern in the resin but it is insufficient to do more than very barely ripple the glass.

Then the samples were reheated and quenched in water at various temperatures, 200-210°F and 150-160°F. Intense fringe patterns developed both in the bulk resin and in the resin along the filament. Quenching in 150°F water caused fractures to occur in all except the thinnest (#1) piece. Apparently the fractures started at the point of maximum stress concentration

(about 1/4 the width of the piece from the end) and spread toward the center.

As will be explained, the thinnest piece only a tenth of an inch thick is a special case. In one of the thickest samples, fracture occurred at both ends, one fracture being relatively small.

The overall strain development when cooled before fracture is shown in Figure A-10. Note the ripples and heavy fringe patterns on either side of a less heavily strained center. The multiple fringe patterns at the points of stress concentration are given in Figure A-11. The fracture occurs at a point. It can be in the resin as in sample 3 (Figure A-12) as a vertical crack extending at right angles to the microtape at a point about 1/4 the thickness of the piece inside the end. It can be a shear peeling fracture (Figure A-13) that separates the bulk resin from the flat side of the microtape. It can even be a break in the microtape (Figure A-14) that relieves the separation of the microtape from the resin before it gets started. We examined this latter case rather carefully (Figures A-15, A-16 and A-17). Figure A-15 shows an edge view at 50X with the highly developed fringe pattern to the right on the broken side of the split, the split in the microtape with the straightened-out broken microtape ends and the lower order fringe pattern to the left extending toward the center of the piece. Figures A-16 and A-17 are at 25X. Figure A-16 is a view of the rippled flat side of the tape. Figure A-17 is a view taken at an angle to show the failure region as dark.

When the resin layer on either side of the microtape was 0.05" or less (the #1 piece), the piece was too narrow to develop a stress concentration at the ends. Instead, it acted as if it had infinite length and rippled to produce relatively low order fringe patterns (Figure A-18). The severe quenching (150°F) from 350°F that failed the thicker pieces did not fail the piece 0.10" thick.

It is very difficult to analyze the fringe patterns looking down the rippled microtape from the end of the specimen. We were looking for evidence of stress concentration around the periphery of the tape. By looking at an angle to the microtape at 50X with double polarized light, we were able to pick up this pattern (Figure A-19) which is indicative of stress concentration at the corners. This indication, although hard to see, would be intensified in a closely-packed circumferentially-wound structure and may be the reason for the low failure values in the tubes made to date.

TABLE A-1

Resin Shrinkage vs. Buckling of Single Microtape Filament

Cure Schedule: 1/2 hr. 200°F
 1/2 hr. 250°F
 1/2 hr. 300°F

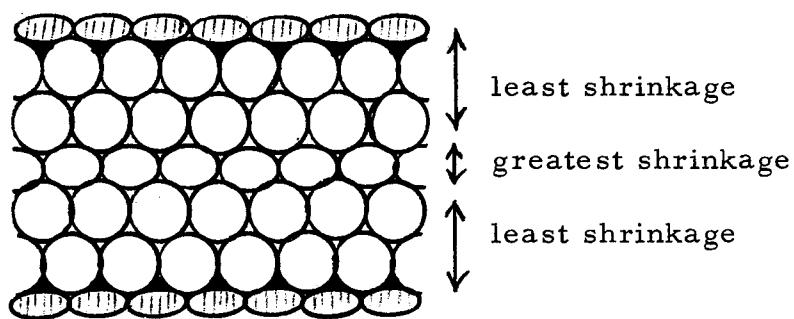
| <u>Sample No.</u> | <u>Cross Section Area, sq. in.</u> | <u>Length of Piece</u> | <u>Thickness of Piece</u> | <u>Specific Gravity of Polymer Only</u> | <u>Shrinkage Based Only on Polymer</u> | <u>Buckled by Stress</u> |
|-------------------|------------------------------------|------------------------|---------------------------|-----------------------------------------|----------------------------------------|-------------------------------|
| 1 | .0318 | .943 | .109 | 1.2303 | 2.64 | None |
| 2 | .0705 | .768 | .235 | 1.2294 | 2.56 | None |
| 3 | .0836 | .915 | .275 | 1.2315 | 2.73 | None |
| 4 | .1137 | .870 | .322 | 1.2323 | 2.79 | High amp. buckling 1/3 length |
| 5 | .1636 | .665 | .376 | 1.2322 | 2.78 | High amp. buckling 2/3 length |

Cure Cycles for Cast Resins

| <u>A</u> <u>Epoxy-Anhydride</u> | <u>B</u> <u>Epoxy-Amine</u> | <u>C</u> <u>Polyester</u> |
|------------------------------------|--------------------------------|------------------------------|
| 30 min. @ 150°F | 30 min. @ 150°F | 30 min. @ 150°F |
| " " " 200°F | " " " 200°F | " " " 200°F |
| " " " 250°F | " " " 250°F | 180 " " 250°F |
| | 180 " " 300°F | |

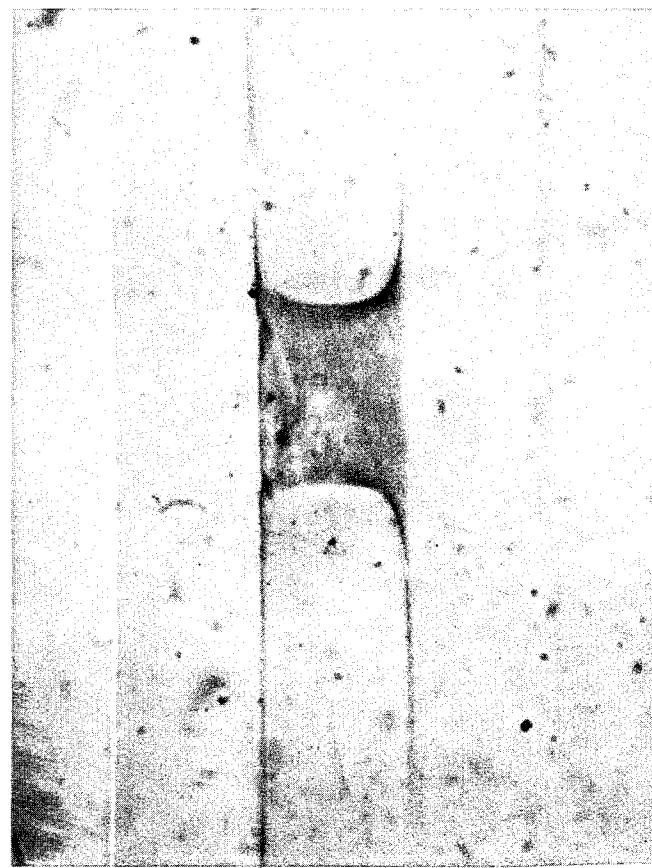
FIGURE A-1

Diagram Using Micelles of a Resin Layer Between
Microtape Illustrating Considerable Deformation
May Be Expected in Middle Layer



Micelles

- Glass
- Coupling Agent
- Non-deformed Resin
- Deformed Resin

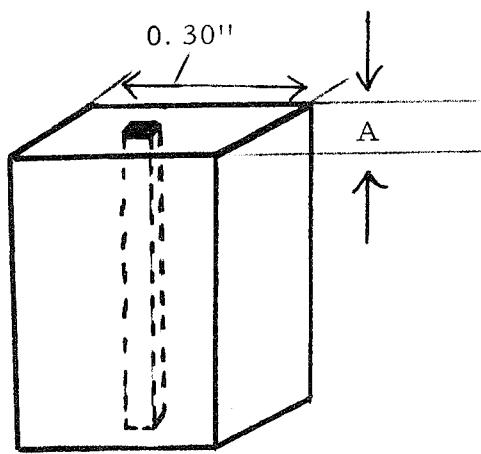


← .00165

FIGURE A-2

Photomicrograph 60X Magnification Showing
in Cross Section the Resin Between Adjoining
Winds of Microtape

FIGURE A-3



Resin Castings Around One Microtape

Dimension A - 0.12'', 0.23'', 0.28'', 0.32'', 0.50''

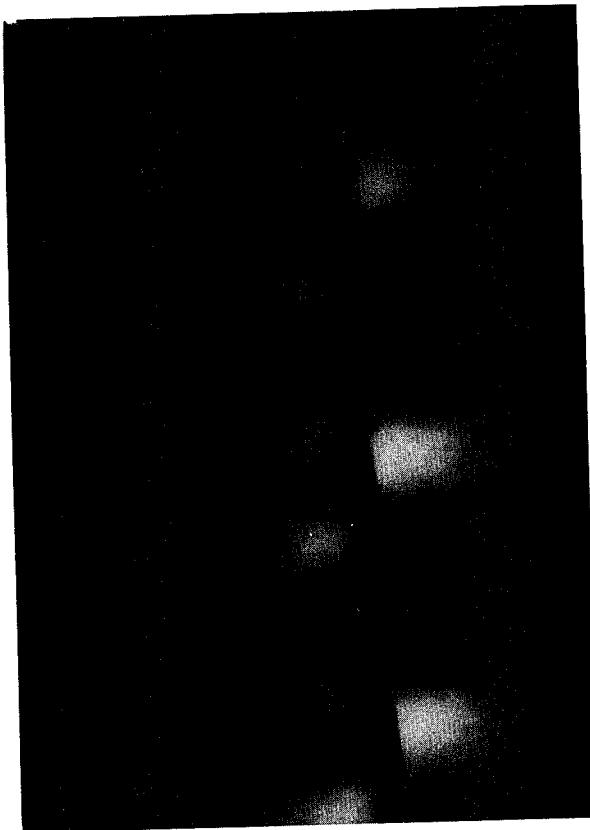


FIGURE A-4a

Casting (100X) Low Strain in
the Resin Bonded to the Wide
Surfaces of Microtape
(Polarized Light)

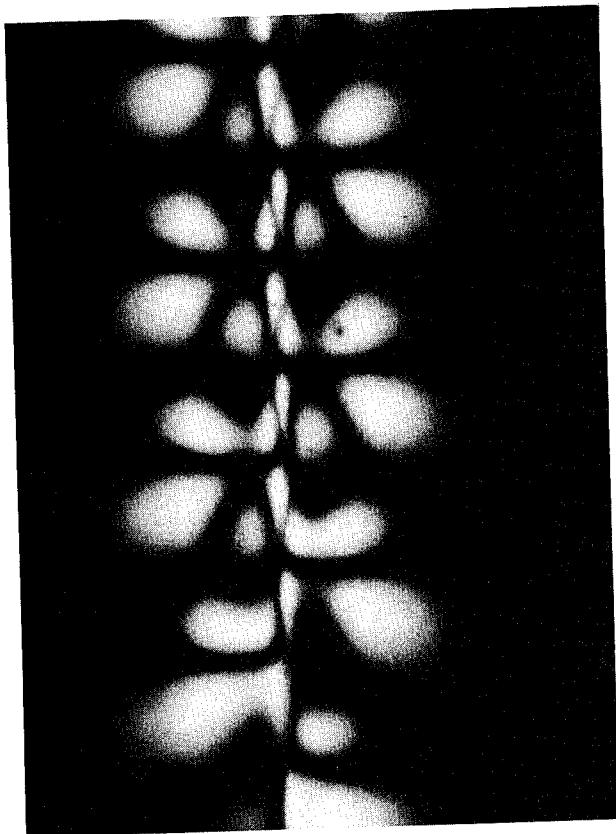


FIGURE A-4b

Casting (100X) Medium Strain
in the Resin Bonded to the
Wide Surfaces of Microtape
(Polarized Light)

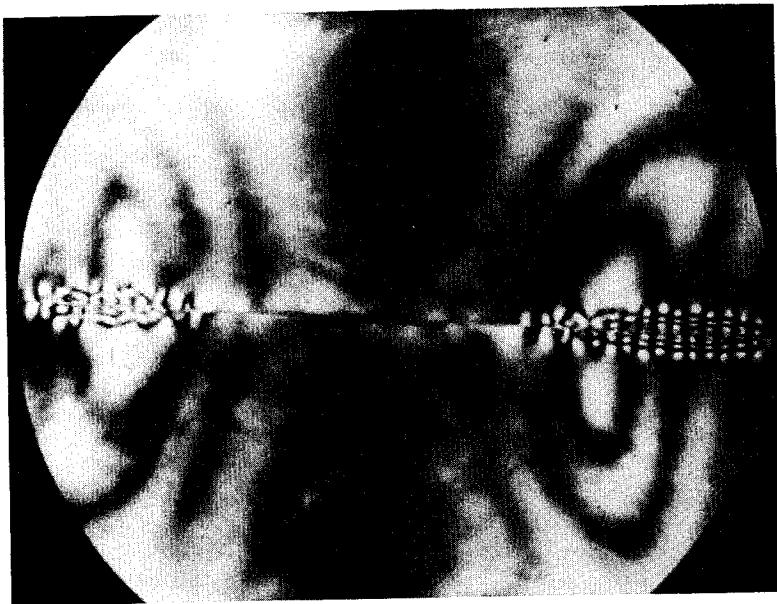


FIGURE A-5b

Same Casting But Viewed at Center to Show Duplication of Patterns at Either End and Relation to Overall Pattern in Resin

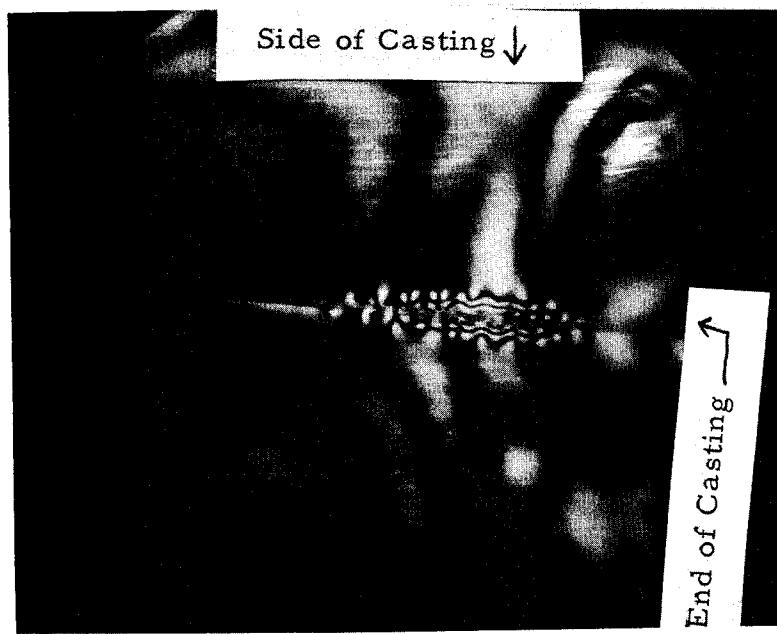


FIGURE A-5a

Casting Viewed with Polarized Light to Show Stress Concentration in Resin Around Microtape and Relation to Surface Geometry

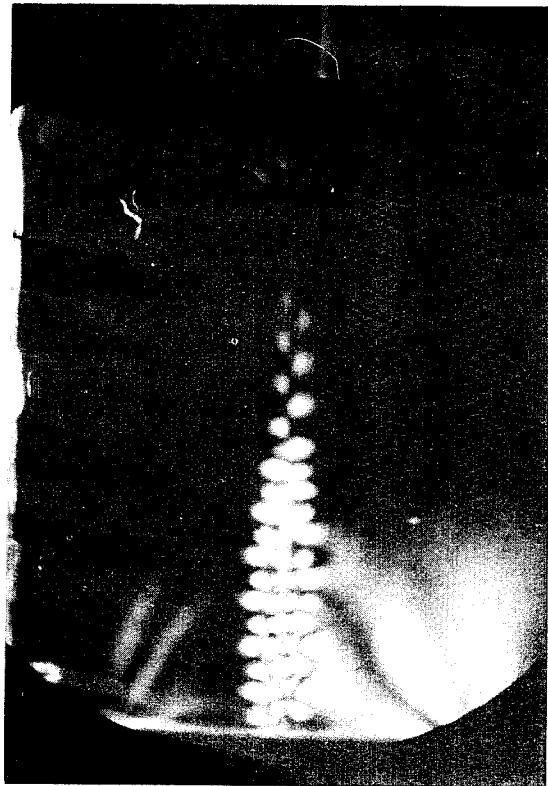


FIGURE A-7a

Illustrates the Effect of More
Further Curing at 300°F

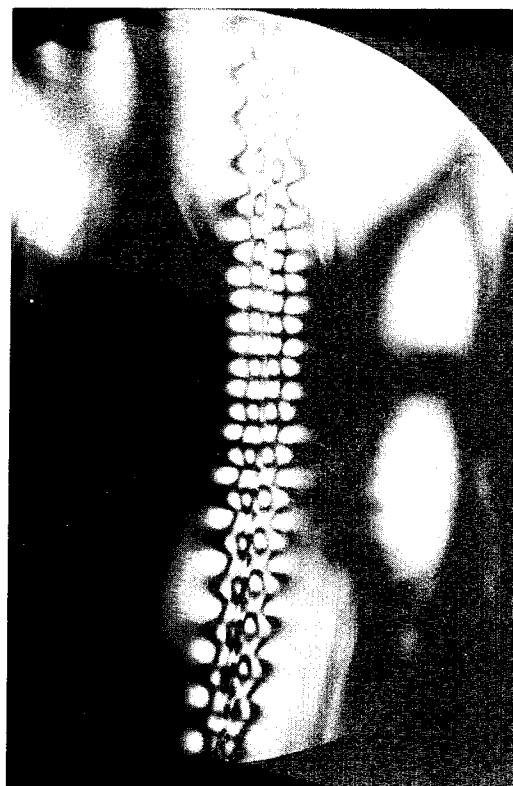


FIGURE A-7b

Another Illustration of Further
Curing at 300°F. Note More
Fringes on Either Side of Center

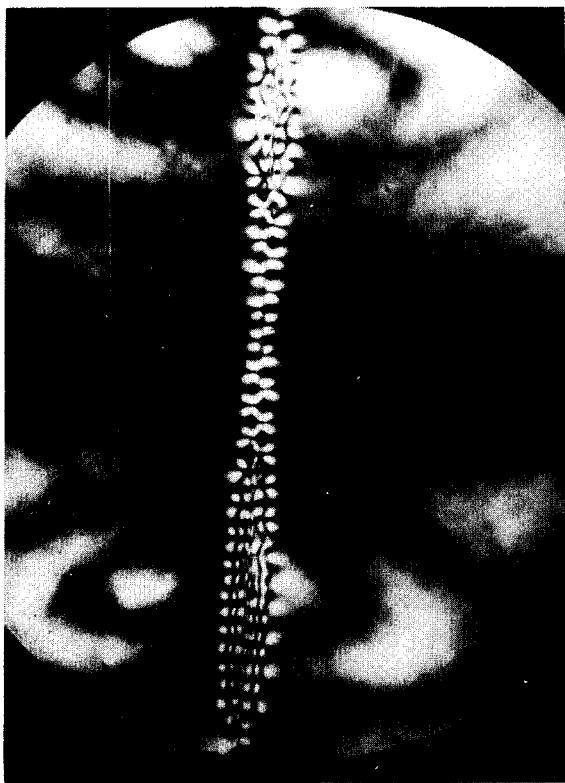


FIGURE A-8

Casting 3/8" Thick Air Cooled
from Stabilization at 350°F

↓ End of Casting



FIGURE A-9

Casting Cooled in Insulated
Blanket After Being Reheated
to 350°F to Stress Relieve



FIGURE A-10

Strain Pattern Obtained by
Stabilizing 3/8" Thick Casting
at 350°F and Quenching in
Water at 150°F



FIGURE A-11

End of Same Casting as Fig. A-10
Showing High Strain Region in
Resin Surrounding Microtape and
Supplementary Patterns in Bulk
Resin

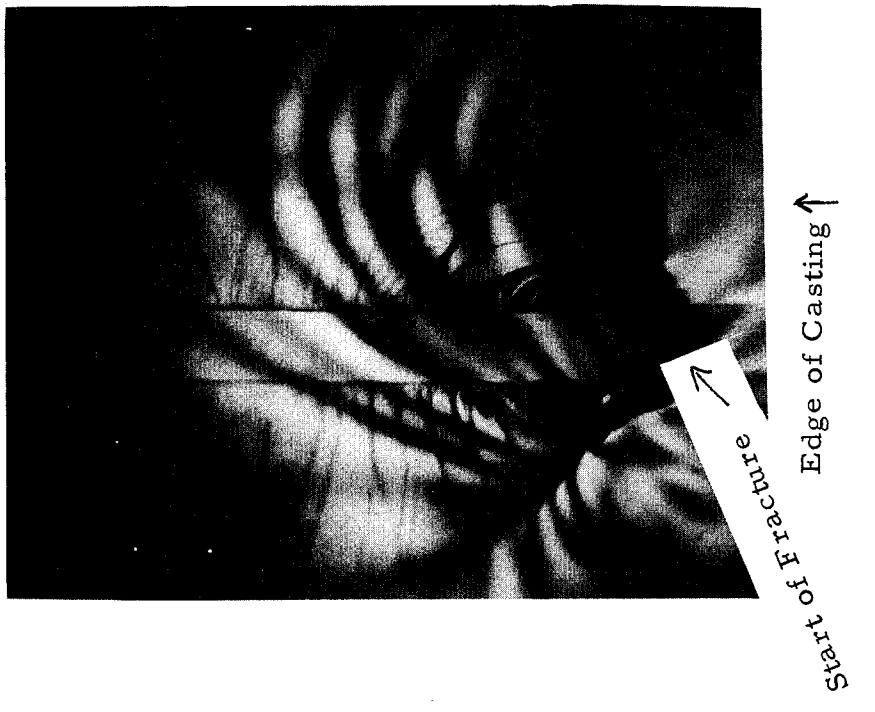


FIGURE A-12

Failure in Resin at Point
of Maximum Stress Con-
centration

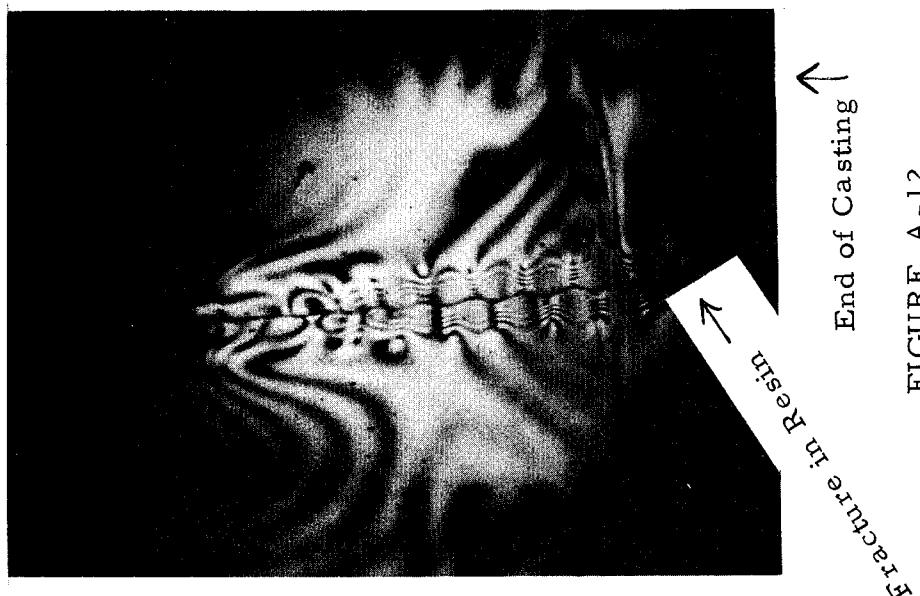


FIGURE A-13

View Showing Flat Face of
Filament Indicating Separa-
tion of Resin from Face



End of Casting ↑

FIGURE A-14

Failure of Resin at Glass Bond
and Failure (black line) of Glass
Due to Bending and Brittleness;
Polaroids not Fully Crossed



FIGURE A-15

50X Magnification Side View
of Fractured Microtape in
Casting Figure A-14

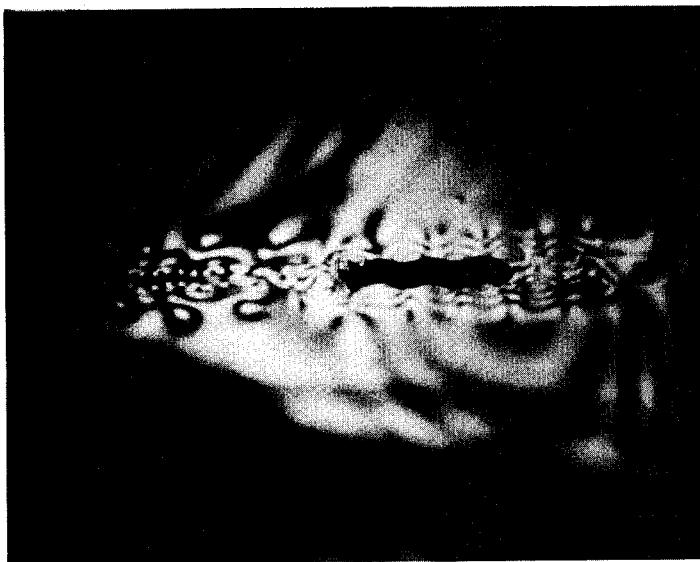


FIGURE A-17

Angle View of Figure A-14;
Polaroids Fully Crossed

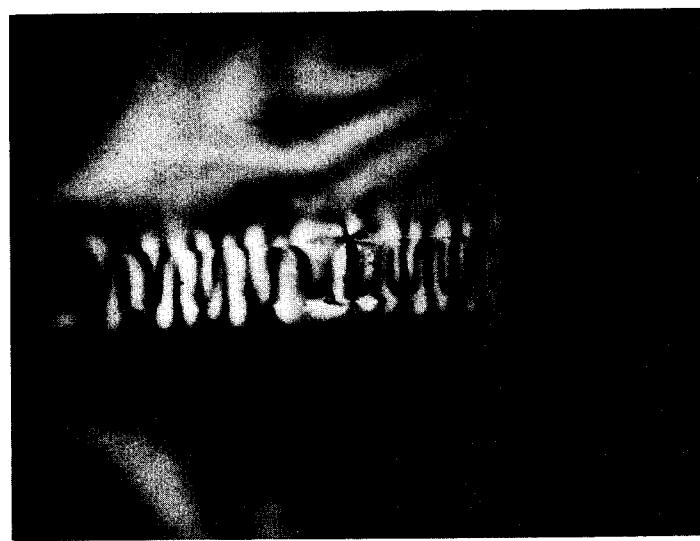


FIGURE A-16

Flat Side View at 25X of
Figure A-14

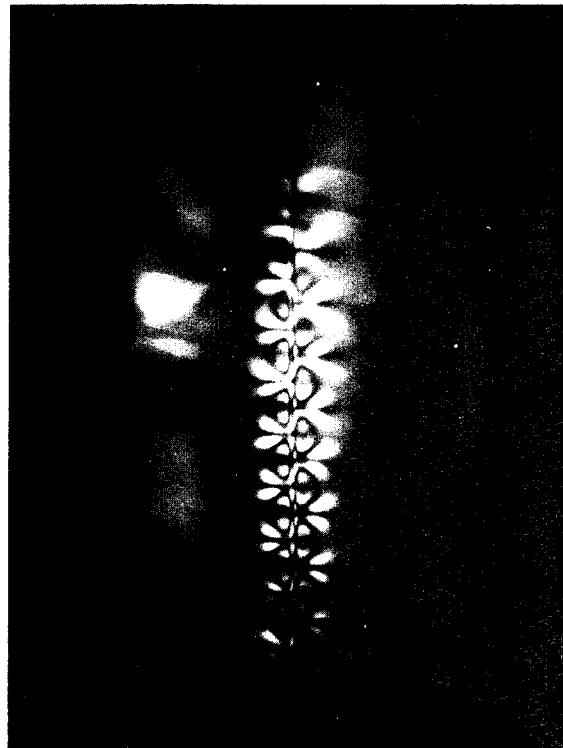


FIGURE A-18

Strain Pattern (25X) Developed in
0.105" Thick Casting Stabilized in
Cure at 350°F and Quenched in
Water at 150°F



FIGURE A-19

Looking at a Ripple of Microtape
in a Casting in Cross Section to
See the Variation in Strain Pattern
(50X)

APPENDIX B

Shrinkage and External Loading: Its Effect on Water Absorption in Castings

In our previous program, sufficient work was done to suggest that a relationship existed between external loading of a cured resin block and the water it would absorb if immersed under loading in water at room temperature. During this contract, work was continued using longer time intervals for immersion and a greater variety of resin formulations (see Table II). The information obtained is summarized in the following paragraphs.

The densities and shrinkage on curing calculated from the densities in Table II indicate that usable epoxy and polyester systems have a wide variation in shrinkage. Generally, a different size of casting of the same formulation will generate significantly different density materials. This is due likely to the exotherm generated on curing as discussed earlier in this report. However, at least one resin system exists that has low shrinkage on curing and is not affected by size differences within the range studied (E-828, 91 pph MNA, 0.6 pph BDMA).

In the two different epoxy resin systems studied, one reached a degree of equilibrium within a reasonable time; but the other, the high shrinkage system, continued to rapidly gain (5% in 40 days) in water (Figure B-1). There appeared to be a general relationship between shrinkage and water absorption;

the higher the shrinkage, the greater the water absorption. This observation would indicate there is a relationship between internal stress that is generated by shrinkage and water absorption.

When compressive force was applied at 30% of ultimate loading, the resin whether showing relatively high or low unloaded absorption was restrained in the amount and rate of water absorption. This shows there is a relationship between applied stress and water absorption (Figure B-2).

When long terms of immersion are used, ambient differences become evident. Figure B-3 shows the effect of the summer vs. the winter temperatures (80 - 85°F vs. 70°F ambient). The low shrinkage resin epoxy - 91 pph anhydride stabilizes at 1.2% after 30 days at 70°F. However, at 80 - 85°F, stabilization occurs in 45 days at 1.6%, a 33% increase in absorbed water for only 10-15° rise in temperature. Even inside, it is reasonable to expect this difference in summer and winter temperature!

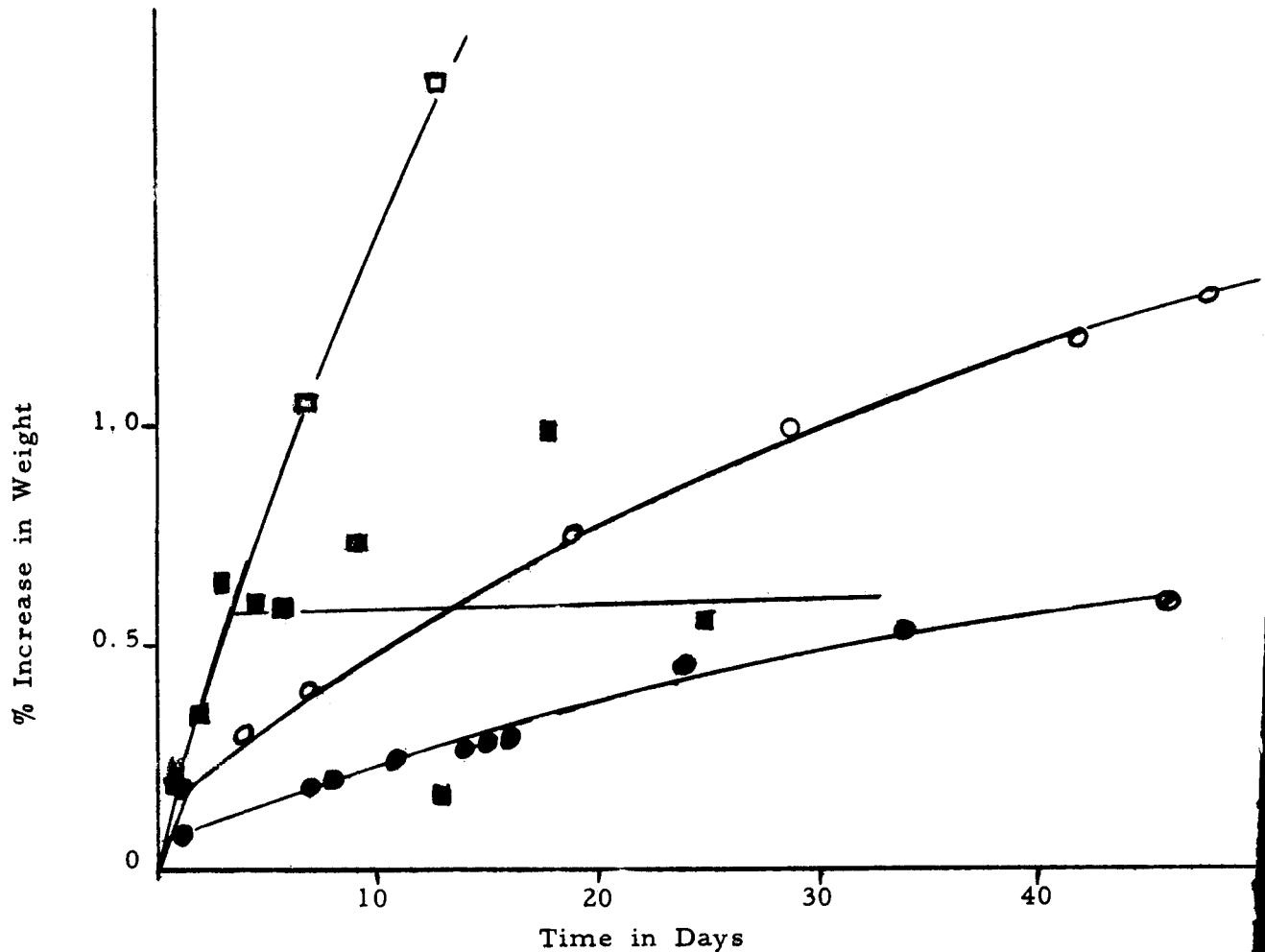
Data (Figure B-4) have also been obtained with the epoxy - 91 pph anhydride resin as the 1/8" x 1/8" x 1/4" blocks in an unloaded and a 3500 psi load condition over a long term. The resulting curves show that the loading at 3500 psi delayed but did not stop absorption. Previous work with cylinders of similar size with the same resin showed no effect at this degree of load but considerable at twice this load. The absorption at double the load was only one-third the "no load" value.

A comparison of solid cylinders and blocks of about the same size undergoing water soak under summer ambients is given in Figure B-5. Since the blocks and cylinders both have the same shrinkage, the observed effect strongly suggests that the shape factor is important in absorption.

Evidently the cylindrical shape will develop more restraint and resist water penetration than that of the block shape. The swelling in the block is greater, possibly by 30%, than that of the cylinder. The same effect is found with the epoxy - 41 pph anhydride resin. The block absorbs possibly 50% more water than the cylinder (Figure B-6). Note that it is the anhydride component with its $\text{C}=\text{O}-\text{O}-\text{C}$ group that is responsible for water absorption, even though the anhydride is low, as in this resin formulation.

These data suggest that the shape factor of the matrix may be critical to control swelling of the matrix even when the matrix is not bonded to the filament. It is also likely that, as swelling occurs in the resin surrounding although not necessarily bonded to the filaments, the resin becomes restrained and the passage of water to the filament surface may be greatly reduced. This analysis presumes that the resin does not fracture at the filament surface.

FIGURE B-1
WATER ABSORPTION VS. TIME
 (Room Temperature)
 (No Loading)



Castings

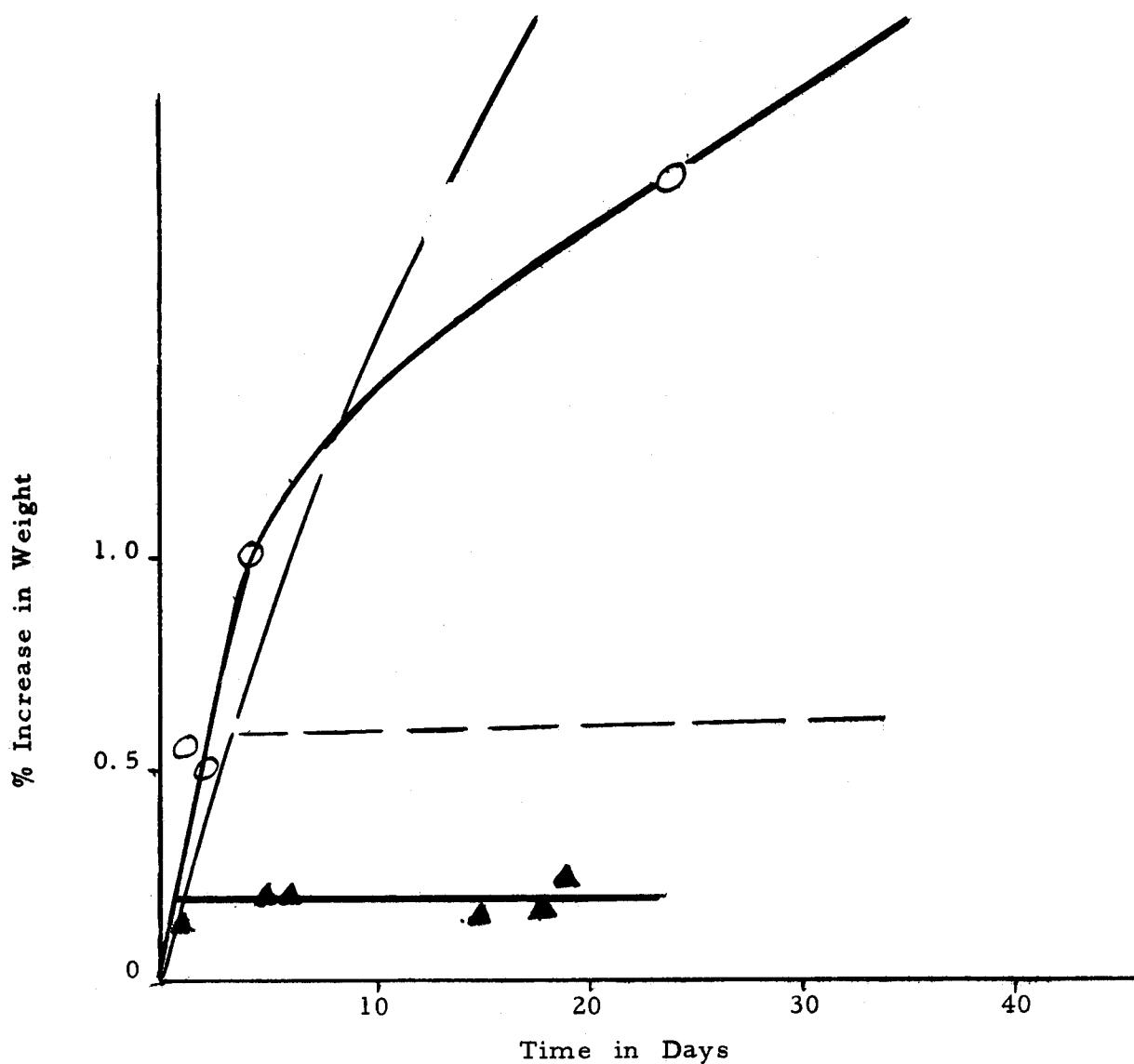
ERRA-0300, 28.7 pph MPDA
 1/8" dia. x 1/4" □
 1/2" x 1/2" x 1" ○

E-828, 91 pph MNA, 0.6 pph BDMA
 1/8" dia. x 1/4" ■ *
 1/2" x 1/2" x 1" ●

* the bulk of the data indicates a flat almost horizontal line from two days onward

FIGURE B-2

**The Effect of Compressive Loading on Water Absorption
at Room Temperature**



Compressive Load - 7300 psi

Casting Size - 1/8" dia. x 1/4" long

1. ERRA-0300, 28.7 pph MPDA ○
2. E-828, 91 pph MNA, 0.6 pph BDMA ▲

The long dashed line is the "no load" absorption for Formulation 1;
the short dashed line for Formulation 2.

FIGURE B-3

Castings - Weight Gain vs. Time - Effect of Water Temperature, No Load

Resin: E-828, 91 pph MNA, 0.6 pph BDMA

Shape: 1/8" x 1/8" x 1/4" Blocks

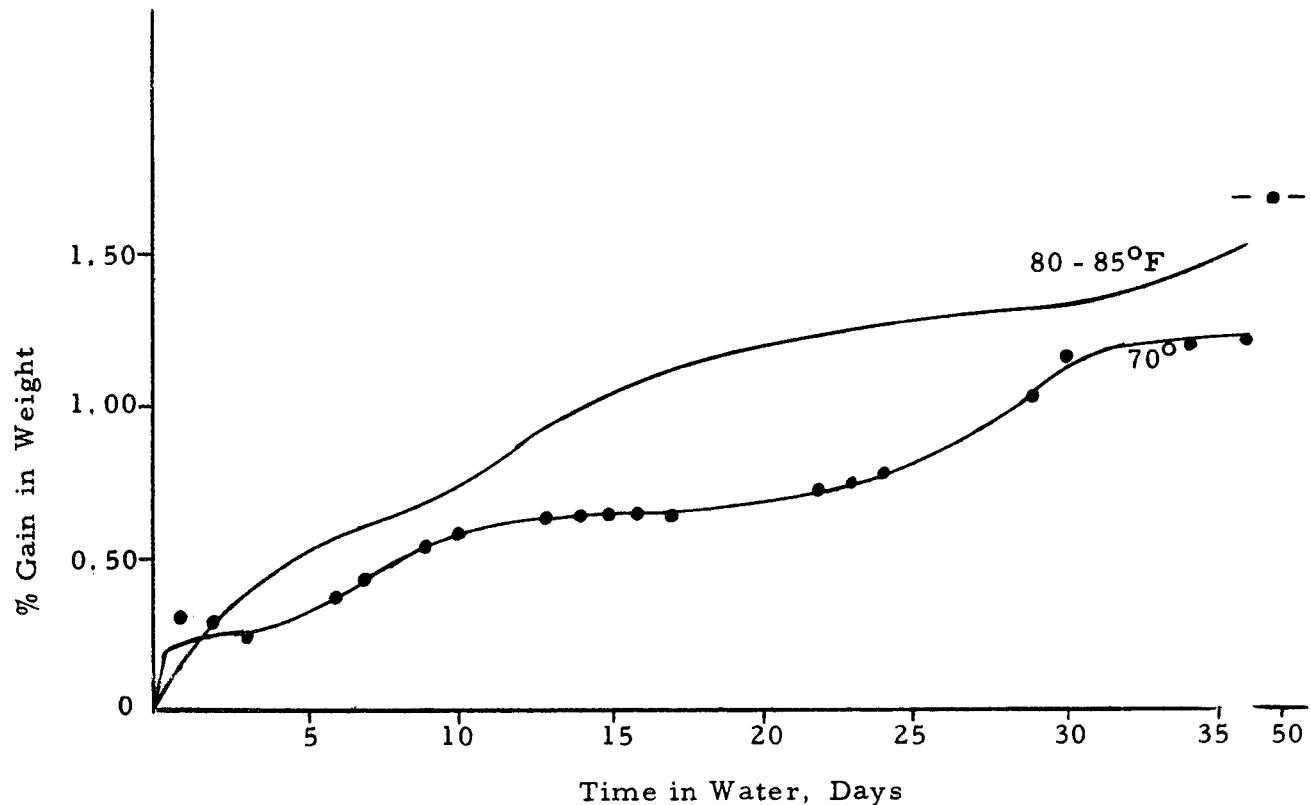


FIGURE B-4

Castings: Weight Gain Vs. Time Under Load

Resin: E-828, 91 pph MNA, 0.6 pph BDMA

Shape: 1/8" x 1/8" x 1/4" Blocks

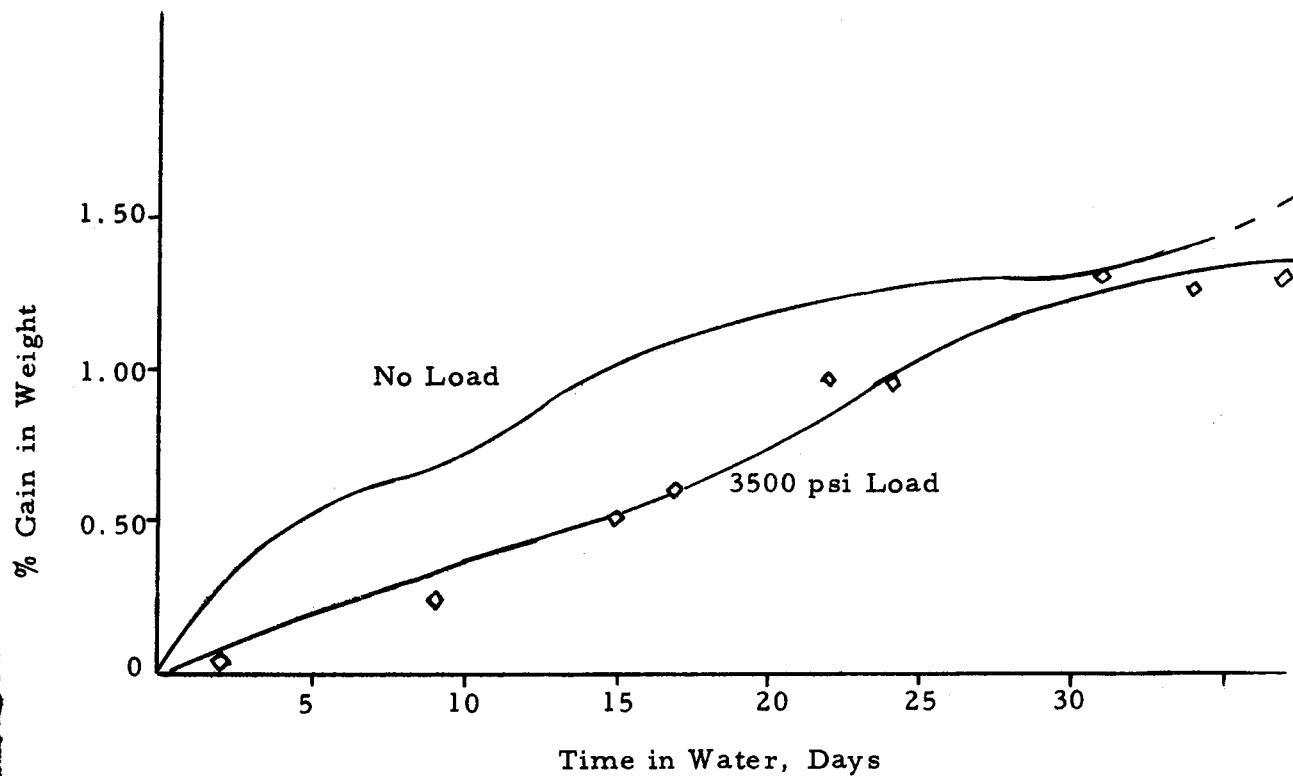


FIGURE B-5

Castings: Weight Gain Vs. Time in 80 - 90°F Water

Resin: E-828, 91 pph MNA, 0.6 pph BDMA

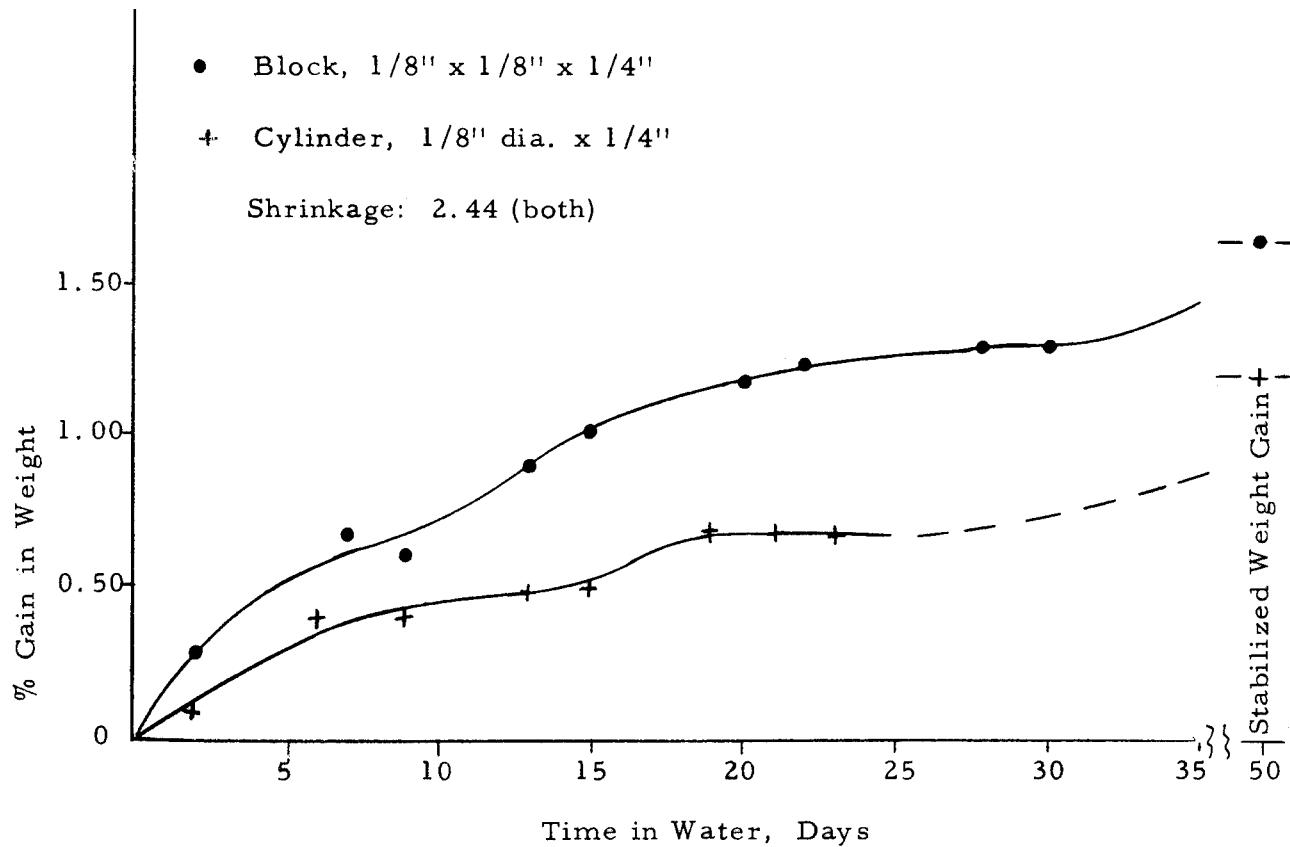
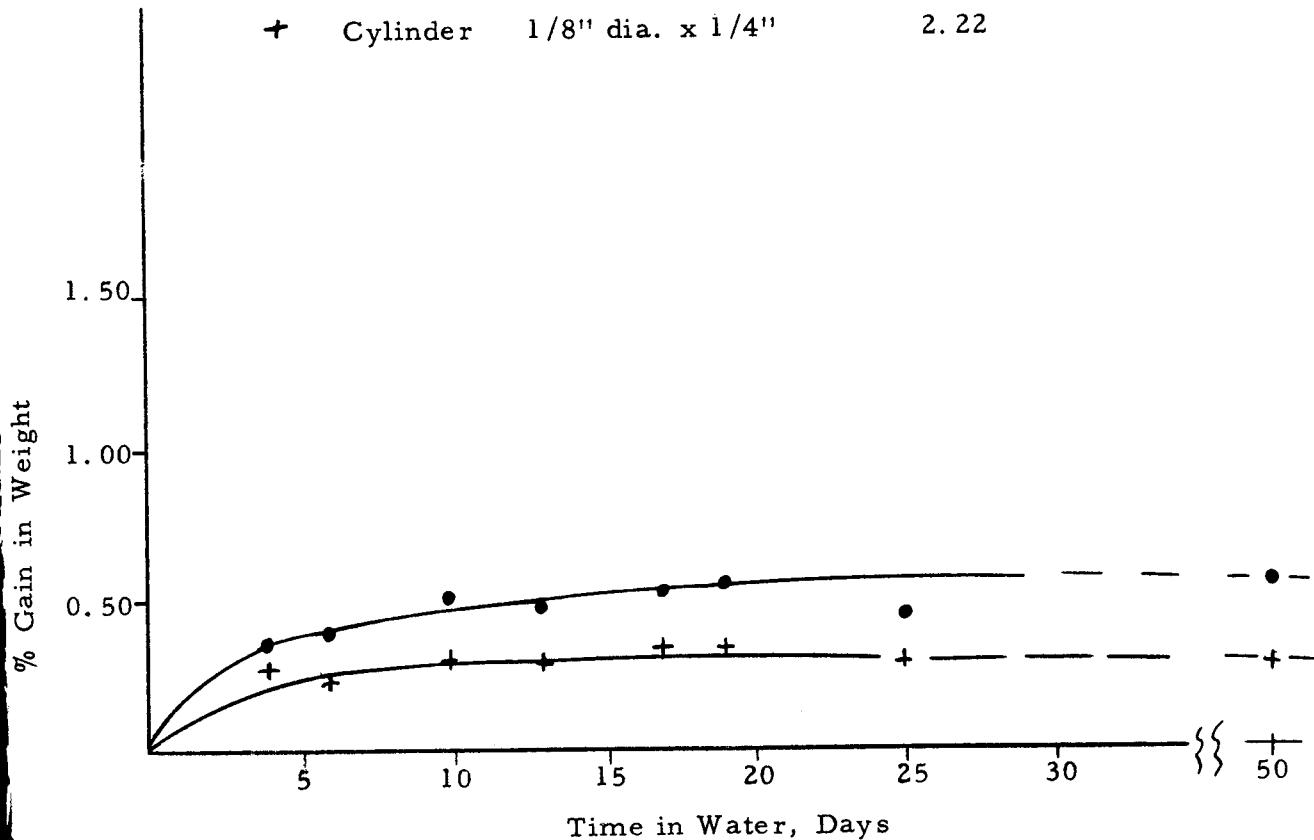


FIGURE B-6

Castings: Weight Gain Vs. Time in 80 - 90°F Water

Resin: E-828, 41 pph MNA, 0.6 pph BDMA

| | <u>Shape</u> | <u>Size</u> | <u>Shrinkage</u> |
|---|--------------|--------------------|------------------|
| • | Block | 1/8" x 1/8" x 1/4" | 1.41 |
| + | Cylinder | 1/8" dia. x 1/4" | 2.22 |



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